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**INVESTIGATION OF ELECTROPLATING PROCEDURES FOR
MAGNESIUM LITHIUM ALLOYS**

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ABSTRACT

Methods for electroplating magnesium lithium alloys, LA-141, and LAZ-933, were investigated, and the corrosion aspects of the resultant electroplates were evaluated by using accelerated laboratory and outdoor exposure tests.

A method was found that produced plating adhesion comparable in strength to that produced on magnesium alloy AZ31B which was used as a comparison. This plating adhesion was evaluated on the basis of results of conventional qualitative tests (bending, scraping, and heating) and also on the results of tests conducted to determine quantitatively the bond strength of the coating. This plating method consisted of pickling the alloy in a nitric acid solution, then treating in a modified (low pH) "Dow" zincate bath, and finally electroplating by conventional methods.

Plated coatings produced by this method provided a moderate amount of corrosion protection from a high humidity environment, but considerably less protection from a salt spray environment. The coatings also provided a fair amount of corrosion protection when exposed to an outdoor (MSFC) environment.

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. RESEARCH AND DEVELOPMENT OPERATIONS

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INVESTIGATION OF ELECTROPLATING PROCEDURES FOR MAGNESIUM LITHIUM ALLOYS

SUMMARY

Methods for electroplating on magnesium lithium alloys, LA-141 and LAZ-933, were investigated. Acid pickle and activators commonly used to prepare standard magnesium alloys for plating did not adequately activate surfaces of these magnesium lithium alloys for subsequent zincate treatment and plating. Other methods did, however, produce electroplates on these alloys with plating adhesion that was comparable in strength to that produced on magnesium alloy AZ31B which was used for a comparison. This plating adhesion was based on the results of conventional qualitative tests (bending, scraping, and heating) and also on the results of quantitative tests made to determine the bond strength of the coating. The method that produced the most favorable results consisted of pickling the alloys in a 6 percent solution of nitric acid, treating for 10 to 12 minutes in a modified (pH 7.5-8.0) "Dow" zincate bath, and electroplating by conventional methods.

In addition to the adhesion tests noted above, plated coatings produced by this method were evaluated for their corrosion protection and compared with the corrosion resistance of electroplated AZ31B alloy. The test environments included a 5 percent salt spray, an environmental test chamber (high humidity), and an outdoor site at MSFC. Test panels were plated with either gold, cadmium or nickel. The results of these corrosion tests showed that electroplated coatings on the magnesium alloys provided very little protection from these environments unless the electroplates were of sufficient thickness to eliminate porosity. In certain cases where plating porosity was not eliminated, corrosion of test panels was actually accelerated by the plated coating.

INTRODUCTION

Because of their high strength-to-weight ratio, magnesium alloys, in general, have become important for use in light weight structures. More recently, magnesium lithium alloys, LA-141 and LAZ-933, which are relatively new materials, have become even more important for light weight aerospace use since they are lighter than conventional magnesium alloys (for example, LA-141 is approximately 25 percent lighter) and

also because they exhibit good stiffness-to-weight ratio. Magnesium lithium alloy LA-141 contains approximately 14 percent lithium and 1 percent aluminum by weight, while LAZ-933 has about 9 percent lithium, 3 percent zinc, and 3 percent aluminum. The high lithium content of these alloys helps to give them their extreme lightness, but unfortunately, because of its high chemical reactivity, the presence of this element imposes some undesirable characteristics. The alloys exhibit very poor resistance to corrosion, and hence, for most applications, it is necessary to apply a corrosion protective coating. In addition to making the alloys more susceptible to corrosion, the high lithium content has somewhat hindered attempts to successfully apply protective coatings.

There are a number of chemical type treatments in common use for the corrosion protection of conventional magnesium alloys, some of which have recently been successfully applied to magnesium lithium alloys. Also, several reported attempts have been made to electroplate these alloys with varying degrees of success. Probably the first attempt was the use of the conventional "Dow Chemical" process for plating on magnesium alloys. It was reported that the immersion zincate deposits did not adequately adhere to these alloys when this process was applied. Some degree of success, however, has been reported as a result of the modification of certain phases of the "Dow Chemical" process, but to date, no method has been reported that produced quality electroplates on these magnesium lithium alloys with a degree of consistency that is acceptable or equal to platings applied to conventional magnesium alloys.

The three most common and widely used methods for applying metallic coatings to the standard magnesium alloys include (1) immersion zinc plating, (2) electroless nickel, and (3) direct electroplating of nickel. After the initial layer of zinc or nickel is deposited, other metals can then be electroplated over the initial layer. Of these three methods, perhaps the most common and commercially accepted is the zincate method. In this method, a very thin film of zinc is chemically deposited on a cleaned and activated magnesium surface, and then a copper "strike" is applied over the zinc. As stated above, other metals are then applied to desired thicknesses over the copper. This report describes several phases of work that were undertaken in an effort to improve existing procedures or to establish new plating procedures for the magnesium lithium alloys. The conventional "Dow" zincate method, incorporated with various pre-cleaning and "activating" techniques, was, for the most part, the basis of this study. Some effort, however, was spent on other plating methods.

EXPERIMENTAL PROCEDURES

Test specimens of LA-141 and LAZ-933 magnesium were prepared and plated by various techniques and these plated specimens were compared with similar plated specimens of conventional magnesium alloy AZ31B. Cleaning, activating, and plating techniques were evaluated on the basis of the quality of the resultant electroplate. Generally, the quality of such deposits was assessed by one of the following methods:

- a. Qualitatively testing the adhesion by bending and/or prying the coating with a sharp instrument.
- b. Quantitatively measuring the coating - substrate bond strength by soldering or adhesively bonding two plated specimens and then testing in a tensile machine.
- c. Subjecting plated specimens to accelerated and atmospheric corrosive environments.

Panels of alloy LA-141, 1 inch by 3 inches by 0.060 inch, were used in the preliminary study to determine the degree of acceptability of the plating adhesion. This alloy was used in most of the experimental work because it was considered to be the most difficult of the two magnesium lithium alloys to electroplate. Hence, alloy LAZ-933 will not be discussed in this phase of the report. If an experimental method appeared to show some promise, based upon the results of a qualitative adhesion test using these small test panels, then larger test panels, and finally 1 inch by 4 inch blocks, were plated in an attempt to quantitatively measure the bond strength of the coating by the method previously described.

Precleaning of all specimens consisted of degreasing by wiping with acetone and soaking for 10 to 20 minutes in an alkaline cleaner. Prior to the final zincating or plating step, a fairly wide range of acid pickling and activating baths were used which will be discussed later.

After activation, specimens were treated in a zincate bath (this bath was used only in the preliminary attempts to plate this alloy) of the following composition [1]:

Tetrasodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) - 16 oz/gal

Zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) - 4 oz/gal

Sodium fluoride (NaF) - 0.67 oz/gal

Sodium carbonate (Na_2CO_3) - 0.67 oz/gal.

The pH range (electrometric) of the bath was 10.2 to 10.4 and the bath was operated at a temperature of 175° - 185°F (79° - 85°C).

After the zincate treatment, the specimens were rinsed and copper plated in a bath of the following composition [1]:

Copper-cyanide (CuCN) - 5.5 oz/ gal

Potassium cyanide (KCN) - 9.0 oz/gal

Potassium fluoride (KF) - 4.0 oz/gal.

This bath was operated at a pH range of 9.6 to 10.4 and at a temperature of 130° - 140°F (54° - 60°C). The initial current density employed was 5 amps per square foot (ASF) which was gradually increased to 20 ASF.

DISCUSSION OF RESULTS

Due to the heavy mill scale that was present on the LA-141 stock material, it was necessary to either remove the scale mechanically and/or by pickling in an acid bath. In the initial attempt to prepare the surface of this alloy for plating, the scale was removed prior to activating by pickling for 1-3 minutes in a bath containing 50 ml of 70 percent nitric acid in a liter of water. Later in the program, specimens were machine sanded to remove the scale and, in some cases, pickled in the above listed nitric acid also. However, in this case, the time required in the pickling bath was reduced considerably. In all cases, prior to any activation treatments, the mill scale was first removed by one or both of the methods described above.

Activation and Pickling Treatments

Hydrochloric acid activation. The initial attempt to prepare the surface of alloy LA-141 for plating, after scale removal, consisted of activating the surface for 30 seconds to 1 minute in a 0.7 percent solution of hydrochloric acid in water. Specimens were then zincated for seven minutes and copper plated for 10 minutes in the previously described zincate and copper baths. Several attempts using this and various hydrochloric acid concentrations resulted in very poor adhesion of the copper plate to the basis metal.

Hydrofluoric - nitric acid activation. The surfaces of additional panels were prepared by activating in various concentrations of hydrofluoric acid and mixtures of hydrofluoric and nitric acid. Subsequent plating by the zincate method resulted in somewhat better adhesion than that obtained with hydrochloric acid activated surfaces, but the adhesion was still not considered acceptable. Varying the time in the activating baths and in the zincate bath, as well as varying the current density of the subsequent copper plating bath, resulted in plating adhesion that varied from fair to poor. Upon examination of test specimens after each step in the sequence of operations, it was noted that the specimens that exhibited the poorest plating adhesion also had previously shown zinc deposits that were non-uniform in appearance (light striations and silver colored spots). Further observations showed that this type of zinc deposit was produced only on those specimens that also exhibited a non-uniform appearance after the acid activation treatment. These occurrences suggested that: (1) the magnesium alloy LA-141 surface contained imperfections or impurities that prevented complete activation; (2) these inactive metal striations did not properly react with the zincate solution; (3) the zincate bath, which was designed for conventional magnesium alloys, was not suitable for magnesium alloy LA-141; or (4) a combination of all three of these conditions. Other investigators, who have used the conventional "Dow" zincate bath in an effort to electroplate magnesium alloy LA-141, have reported similar results. Some of these investigators have attributed the trouble to the relatively high pH (9.5 - 10.1) of the standard zincate bath. Their theory was somewhat substantiated by improved plating adhesion when the zincate was applied from a modified zincate bath with an adjusted pH of 8. The reason, it was stated, that this bath produced a better zincate deposit was because the lowered pH helped to compensate for the excessive alkaline surface (pH 11) that had been observed on freshly cleaned and activated surfaces of alloy LA-141. Although these investigators did report that plating adhesion was improved using the modified bath, this still did not produce bond strengths of a magnitude desired. In view of these reported improvements in the plating adhesion, even though they were slight, a decision was made to attempt such a modified zincate bath with further effort directed toward a more satisfactory acid activation treatment. Consequently, a zincate bath of the following composition and with an adjusted pH of 7.5 to 8.0 was prepared [2]:

Zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) - 30 g/l

Sodium pyrophosphate anhydrous ($\text{Na}_4\text{P}_2\text{O}_7$) - 120 g/l

Sodium fluoride (NaF) - 5 g/l

Sodium acetate crystal ($\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$) - 10 g/l.

The bath was operated at a temperature of 165° - 185°F. (74° - 85°C).

The use of this modified zincate bath, in conjunction with the previously used hydrofluoric acid and mixtures of hydrofluoric and nitric acid pickles, resulted in a zinc deposit that was somewhat more uniform in appearance. However, adhesion of the subsequent copper plate was not significantly improved. After the use of several other variations of these activation acids produced no improvement in coating adherence, a mixture of 7 percent nitric acid and 2 percent hydrofluoric acid (48 percent) by volume finally resulted in a coating of copper that was significantly improved over previous coatings. This improvement was exhibited by the lack of flaking or peeling of the coating when the test panel was bent, and by the lack of blistering when the panel was heated. Several other test specimens plated by the use of this activation treatment and the modified zinc bath were soldered together without the copper blistering. Even though this method showed a distinct improvement over the conventional method ("Dow" zincate bath), further tests showed that there still existed a degree of inconsistency that was not completely acceptable. On occasion, for no apparent reason, a completely undesirable deposit would result. The complete processing sequence, using this method, is listed below:

- a. Vapor degrease by wiping with acetone.
- b. Alkaline clean.
- c. Water rinse.
- d. De-scale either by mechanically sanding or pickling in a bath composed of 50 ml of nitric acid in one liter of water.
- e. Water rinse.
- f. Activate for 10 to 20 seconds in a mixture of 7 percent nitric acid (70 percent) and 2 percent hydrofluoric acid (48 percent) by volume.
- g. Water rinse.
- h. Copper plate as previously described.

In an effort to quantitatively measure, to some degree, the bond strength of the resultant coating from the use of this process, test specimens (1 inch x 4 inch x 0.050 inch) were copper plated, soldered together with a 1/2 inch overlap, and then tested on a tensile machine. The strength at which the specimens failed indicated the strength of the bond between the zincate-copper coating and the base metal, provided this strength was less than the strength of the solder. Results of this test are shown in Table I. As indicated by these results, a considerable amount of variation in the quality of adhesion existed when magnesium

alloy LA-141 was plated by the previously described activation and modified zincate method. It was observed, however, that in the case of the extremely low tensile strength (specimen No.4 - 380 psi) the solder actually failed to a greater extent and not the plating. This also was true; but to a lesser extent, in the other specimens that showed low tensile strengths. Therefore, it should be concluded that the coating bond strength of these particular specimens was somewhat higher than the tensile strength showed and that a better soldering technique should have been developed.

As a quantitative measure of the improvement of plating adhesion obtained with the low pH zincate bath over that of the conventional "Dow" zincate bath, four similar specimens of this alloy were copper plated with the initial zincate applied from the "Dow" bath. The specimens were soldered and tested as above in a tensile machine. The results of this test are shown in Table II. Although there was not as much variation in the tensile strengths of these specimens, it was obvious, from these results, that a distinct improvement in the bond strength of the coating was achieved by the use of the modified zincate bath over that of the conventional zincate bath.

Several other acid activators and pickles, used in conjunction with the modified zincate bath, were attempted in an effort to electroplate this alloy with a more consistent degree of plating adhesion.

Chromic acid. In some of the previous experiments, using nitric acid as a pickle prior to the application of the zincate, dark spots and/or dark striations were observed on a number of specimens. When the pickle time in this acid was extended to improve the cleaning of the panels, excessive amounts of metal were removed and a rough surface resulted. Since pickling magnesium alloys in hot chromic acid solutions does not significantly change the dimensions of this metal, it was believed that the use of this acid would provide a cleaner and more reactive surface for the subsequent zincate. However, the use of several variations in concentrations and pickle time of this acid resulted in a very poor quality of electroplate. The pickled metal appeared to be clean, but the subsequent coating was non-uniform in appearance, and peeling resulted when the specimens were bent to a 90° angle.

Phosphoric acid. The use of several different concentrations of phosphoric acid resulted in subsequent electroplates that were deficient in plating adherence as evidenced by flaking or peeling when plated panels were bent.

Sulfuric acid. Panels that were pickled in various concentrations of this acid and subsequently plated resulted in plating adhesion that

was still completely unacceptable. Appearance and adhesion were somewhat improved by the use of activating solutions of ammonium bifluoride and mixtures of ammonium bifluoride and phosphoric acid following the sulfuric acid pickle. However, the improvement in the plating adhesion was still not of a magnitude desired.

Ammonium bifluoride anodizing. This anodizing treatment was designed to clean magnesium alloys without dimensionally changing the metal. Previous experience had shown that the treatment, when applied to magnesium alloy 1A-141, produced a surface that appeared to be exceptionally clean, and the apparent film that was formed provided an excellent base for other subsequent coatings. It was thought that the surface produced by this anodizing treatment might be receptive to either a chemical deposit of zinc or a direct electrodeposit. The following procedure was used [3] :

- a. Degrease and alkaline clean as previously described.
- b. Water rinse.
- c. Anodize in a solution of 30 percent ammonium bifluoride by volume, by applying alternating current and increasing the voltage progressively until 110-120 volts are reached; then applying voltage for 45 minutes after the current falls to less than 5 amps per square foot of workpiece surface.
- d. Water rinse.
- e. Zincate and copper plate, or copper plate directly in previously described baths.

The operating temperature of the anodizing bath was 70°-80°F (21°-27°C). The first attempt to plate specimens prepared by this anodizing treatment, using the zincate immersion prior to copper plating, resulted in plating adhesion that, at first, appeared to be good. However, the copper plate was non-uniform in appearance (showed black striations and light areas) with eventual flaking of the coating when the specimen was bent repeatedly. Copper, plated directly over the anodically prepared surfaces, resulted in a more inferior quality of adhesion than the previous zincate - copper plated specimens. The deposits were covered with minute blisters, and peeling of the plating occurred freely upon bending the specimens. Results of further experiments with this anodizing bath and subsequent plating showed that varying the anodizing time (5-30 minutes) did not improve the quality of plating adhesion, either when the zincate was applied first or when copper was plated directly over anodized specimens.

Nitric acid. In the initial phase of this study, results of some preliminary experiments indicated that a fair degree of plating adhesion could be obtained on surfaces that had been prepared only by removing the "scale" in a solution of nitric acid. Also, results of later experiments had shown that surfaces that were activated in mixtures of nitric and hydrofluoric acid were moderately receptive to zincate deposits. In view of this moderate degree of success using these acids as pre-plating pickles and activators, and the somewhat inferior degree of plating adhesion that had resulted from the use of other acid pickles and activators, discussed hereinbefore, it was decided to investigate further the use of nitric acid as an activator or pickle for this alloy.

Panels were pickled in a 5 percent solution (by volume) of nitric acid and subsequently zincated and copper plated. The plating adhesion appeared to be as good as the adhesion that had been obtained when the surface had been activated with mixtures of nitric and hydrofluoric acid. As a further test of adhesion and as a direct comparison of the two different acid treatments, test specimens were pickled in the 5 percent nitric acid bath while others were pickled in a mixture of 5 percent nitric and 2 percent hydrofluoric acids. They were both then given the zincate treatment and copper plated. No significant difference in the plating adhesion could be observed. As a quantitative test of the bond strength, specimens were pickled in the 5 percent nitric acid bath, plated, and lap shear tested in a manner previously described. In this case, however, lapped ends were bonded together with various organic adhesives instead of solder, as was used on the previous lap shear tests. Organic adhesives were used as another method for bonding specimens because those selected were cured at room temperatures and, thus, this alleviated the effects of heat involved when using solder for bonding. The results of this test are shown in Table III.

Upon examination of the bonded ends of the specimens after failure, it was evident that, in each case, the adhesive bonding materials had failed and not the plating. The copper electroplate was still intact and showed no sign of lifting from the substrate. Therefore, these data did not indicate the actual bond strength of the zincate - electroplated coating; they did indicate however, that the coating bond strength was in excess of 1798 psi (strength of the Lefkowitz adhesive).

Several other concentrations of nitric acid were attempted as a pickle for this alloy in an effort to further improve the quality of subsequent electrodeposits. Concentrations that were significantly above or below 5 percent by volume resulted in subsequent plating adhesion that was inferior to that obtained on surfaces that were activated with the 5 percent bath. However, a bath consisting of a 6 percent solution by volume of nitric acid (70 percent) appeared to produce surfaces that were slightly more receptive to the zincate deposit than

the 5 percent bath. Results of qualitative adhesion tests of additional plated specimens using this 6 percent nitric acid bath further indicated that an improvement in the plating adhesion had been achieved. In an effort to demonstrate this improvement quantitatively, additional tensile tests were made. However, in an attempt to produce more accurate test results, a different specimen joining technique was employed. Plated specimens, 1 x 1 x 3 inches, were butted together and either soldered or adhesively bonded and then tested in a tensile machine. Results of these tests are shown in Tables IV and V. Even though there was still some inconsistency in these results, a considerable amount of overall improvement over previous processes was shown.

It appeared that, for the most part, the adhesives failed at these respective tensile strengths and not the coating on those specimens that were joined by this method. Therefore, as in some of the previous quantitative adhesion tests, these values should not be considered the true bond strength of the coating. On the contrary, it appeared that the coating was pulled from the substrate on those specimens that were joined together by the solder method. These values, therefore, should indicate more closely the true bond strength of the zinc-copper electroplate to the basis LA-141 magnesium provided the heat from the soldering process did not effect the bond.

As a means of providing a criteria in evaluating the plating adhesion obtained on magnesium alloy LA-141, test bars of standard magnesium alloy AZ31B, identical to those used in the LA-141 plating experiments, were copper plated by the conventional "Dow" process. The ends of several of these bars were joined together by soldering, and then tested on a tensile machine. The test results are shown in Table VI. The wide variation in these tensile strengths as indicated by the test results was not expected. However, they did furnish somewhat of a basis for comparing bond strengths that were produced on magnesium alloy LA-141.

Corrosion Resistance

As another method of appraising the quality of the electroplate produced on magnesium-lithium alloys, LA-141 and LAZ-933, and determining the degree of corrosion protection provided by the electroplate, specimens of these alloys were electroplated and subsequently exposed to various corrosive environments. Specimens of magnesium alloy AZ31B were also electroplated and incorporated into the corrosion test program for the purpose of providing a criterion in making the evaluation. Specimens, 2 inches by 4 inches by 0.060 inch, of each of the three alloys were either plated with gold, nickel, or cadmium and exposed to three different test environments. These environments included a 5 percent salt spray regulated in accordance with ASTM B117-61, an

environmental test chamber controlled at a temperature of 95°-100°F and a relative humidity of 95-98 percent, and an outdoor site at MSFC in accordance with standard atmospheric testing procedures (ASTM, "Symposium on Corrosion Testing Procedure," pp 35-36, Philadelphia, 1937). Two different groups of test specimens were gold plated to approximate thicknesses of 0.0001 inch and 0.0005 inch while the cadmium and nickel were plated on two different groups of specimens to approximate thicknesses of 0.0005 inch and 0.002 inch respectively. Panels of each alloy were zincate treated and copper "struck" in baths previously described. The zinc was applied to the magnesium alloy AZ31B from the conventional "Dow" bath, and it was applied to alloys LAZ-933 and LA-141 from the modified (low pH) bath. Details of the entire plating procedures were as follows:

a. Degrease by wiping with acetone.

b. Alkaline clean.

c. Water rinse.

d. Pickle magnesium-lithium alloys LA-141 and LAZ-933 for 1-3 minutes in a bath composed of 6 percent nitric acid by volume. Pickle magnesium alloy AZ31B for 1 minute in a bath composed of 0.9 gallon of phosphoric acid (85 percent H_3PO_4) in a gallon of water. Follow this pickle, after water rinsing, by immersion for 30 seconds in an activator bath composed of 1.6 pints of phosphoric acid (85 percent H_3PO_4), 13 1/2 oz. of potassium acid fluoride, and water to make one gallon.

e. Water rinse.

f. Zincate treat magnesium-lithium alloys, LA-141 and LAZ-933, in the previously described modified (low pH) bath for 12 minutes. Zincate treat alloy AZ31B in the previously described "Dow" bath for 7 minutes.

g. Water rinse.

h. Copper strike at a current density of 5 amps/ft² for 1 minute in the previously described bath. Gradually increase the current density to 20 amps/ft² and plate for an additional 5 minutes.

i. Water rinse.

j. Apply additional electroplates as follows:

(1) Gold plate in a proprietary cyanide bath at a current density of 4 amps/ft² [4].

(2) Nickel plate at a current density of 40 amps/ft² in a bath composed of 7 4/5 fl. oz. of hydrofluoric acid (70 percent HF), 4 oz. of citric acid, 16 oz. of basic nickel carbonate, 1/8 oz. of sodium lauryl sulfate, and water to make one gallon[1].

(3) Cadmium plate at a current density of 40 amps/ft² in a proprietary cyanide bath [5].

Groups of each of the three different electroplated panels were then exposed to the three different test environments described above. The results of these corrosion tests are discussed below.

Salt spray. After a total of 4 hours exposure time, all specimens showed severe surface corrosion. No significant difference in the amount of corrosion was observed between the three different alloys for any of the three platings systems (FIGs. 1, 2, and 3). Overall, the nickel plating provided slightly more corrosion protection than the two other plated coatings, particularly around the edges of the panels. Corrosion occurred on all test panels much sooner than was expected and as a result, the early stage of corrosion was not observed. Because of this, and because of the severity of corrosion in such a relatively short period of time, a decision was made to repeat the salt spray tests with specimens plated to greater thicknesses. In this repeat test, the gold was plated to a thickness of 0.0005 inch and the nickel and cadmium to a thickness of 0.002 inch. Other aspects of the test were identical to the first one that was performed. After one hour of exposure time, each of the gold plated alloys again showed severe corrosion, and there was no significant difference in the amount of corrosion shown in either of the three different alloys (FIG 4). A considerable amount of corrosion was also present on the cadmium plated LA-141 panels after one hour exposure but none was observed on the cadmium plated alloys of LAZ-933 and AZ31B. No corrosion was observed on either of the three different alloys that were nickel plated after one hour exposure.

No further salt spray testing was done on the gold plated panels after one hour exposure time, but the nickel and cadmium plated panels were subjected to the salt spray environment for an additional 4 hours. At the end of this test period (5 hours total) the cadmium plated panels of LA-141 alloy showed severe corrosion and considerably more than the cadmium plated alloys of AZ31B and LAZ-933 which showed about the same amount (FIG 5). No significant corrosion was observed at the end of the 5-hour test period on any of the three different alloys that were nickel plated (FIG 6). (In the photograph, the rough appearance of panel edges resulted from high current density areas).

Environmental (high humidity). The results of the environmental corrosion tests showed that some degree of light corrosion was present on all test panels after 24 hours exposure. As exposure time was increased, the amount of corrosion gradually increased on some panels, while others did not change significantly.

After a total of 336 hours exposure time, the gold plated panels of alloy LAZ-933 showed severe corrosion while gold plated panels of AZ31B and LA-141 showed light to moderate amounts of corrosion, but much less severe than that shown on alloy LAZ-933 (FIG 7).

At the end of the 336-hour test period, cadmium plated panels of alloy AZ31B showed essentially no corrosion, while cadmium plated panels of alloys LAZ-933 and LA-141 showed very light corrosion and some discoloration which was about the same on each of the two alloys. Numerous small blisters were also noted on panels of LA-141 and LAZ-933 which was not observed on the cadmium plated AZ31B alloy (FIG 8).

At the end of the test period, nickel plated panels of alloy AZ31B showed essentially no corrosion. Alloy LAZ-933, plated with this metal, showed a few spots of corrosion, while the nickel plated panels of alloy LA-141 exhibited light corrosion that covered the entire panel (FIG 9).

Atmospheric (outdoor). After a few weeks of exposure to this environment, either blisters or some form of light corrosion was observed on all panels except those of alloy AZ31B that were cadmium plated. The gold plated panels were essentially covered with small blisters while most of the other panels showed spots of white corrosion.

As exposure time was increased, the blisters on the gold plated panels burst, the gold partially flaked, and corrosion gradually became worse. After a total of 18 months exposure, the gold plated panels showed severe corrosion and pitting with each alloy exhibiting about the same degree of degradation (FIG 10).

The cadmium plated panels of alloy AZ31B showed essentially no corrosion at the end of the 18 months test period. On the contrary, cadmium plated panels of alloys LAZ-933 and LA-141 were severely corroded. In the case of the LA-141 alloy, the cadmium electroplate was lifted from the substrate and, for the most part, removed from the base metal (FIG 11).

The nickel plated panels showed a considerable amount of corrosion but there was no significant difference in the amount shown on each of the three different alloys (FIG 12). The corrosion was initiated, for the most part, from small blisters that formed in the early stages of the test that gradually burst and consequently exposed the bare metal.

CONCLUSIONS AND RECOMMENDATIONS

Although it was somewhat more difficult to electroplate magnesium-lithium alloys, LA-141 and LAZ-933, than other standard magnesium alloys, it was demonstrated that these magnesium alloys could be electroplated with a degree of plating adhesion that was comparable in strength to that produced on alloy AZ31B. Quality electrodeposits could not, however, be produced with as great a degree of consistency on alloys LA-141 and LAZ-933 as could be produced on AZ31B. This was especially true with respect to the appearance of the electroplate and its resistance to corrosion. Poor quality sheet and plate stock of LA-141 metal alloy (surface defects that do not react readily with acid pickles) was a major hindrance in consistently producing properly activated surfaces and consequently obtaining good quality electroplates. It is believed that, when these defects are alleviated by improved alloy manufacturing processes, the plating of this alloy will be less difficult and good quality electroplates can be produced with a greater degree of consistency.

Acid pickles and activators that are commonly used on standard magnesium alloys did not produce surfaces on magnesium alloy LA-141 that were receptive to subsequent zincate deposits. Although the use of acid activators composed of mixtures of nitric and hydrofluoric acids produced subsequent electroplates with moderately good plating adhesion, a 6 percent nitric acid pre-plating solution prepared surfaces that resulted in electroplates with qualities that were superior to electroplates produced with other acid activators. It was also concluded that the standard zincate bath must be modified when used with these alloys.

Results of the various corrosion tests of the electroplated panels indicated that plated coatings, in most cases, will actually accelerate corrosion on magnesium alloys if the electroplate is not of sufficient thickness. Since magnesium alloys in general, and particularly magnesium-lithium alloy LA-141, are extremely active metals, galvanic corrosion is initiated through the pores of less active electroplated metals. Thus, when these alloys are plated and are subjected to a corrosive environment, it is necessary to plate to thicknesses that alleviate porosity. The rapid corrosion of the plated panels, especially the gold plated panels, that were exposed to a salt spray environment clearly substantiated the need for a thicker coating.

Although a moderate amount of corrosion protection was provided by the electroplates in the less corrosive test environments (high humidity and outdoor), severe corrosion, in some cases, further indicated the need for thicker coatings when magnesium alloys are plated.

Although the quality of the electroplates produced by this method were somewhat more erratic than that produced on conventional magnesium alloys, it appears that magnesium-lithium alloys LA-141 and LAZ-933 can be electroplated in the laboratory with a satisfactory degree of plating adhesion. On the basis of this investigation, the use of a 6 percent nitric acid pre-plating activation treatment used in conjunction with the modified (low pH) "Dow" zincate bath is recommended when these alloys are to be electroplated.

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1. The Dow Metals Products Company, Magnesium Finishing, *ibid*, pp 93-94.
2. IBM, New Technology Report, "Zincate Method for Plating Magnesium Alloy LA-141." (1965)
3. Battelle Memorial Institute, Research Report, "The Development of Magnesium Lithium Alloys for Structural Applications" (Contract NAS8-5049), p B-27 (January 25, 1963).
4. Sel Rex Corporation, "Bright Gold Process", Operating Procedures.
5. E. I. du Pont de Nemours and Company (Inc). "Cadalyte" Operating Instructions for Modern Cadmium Plating.

TABLE I. - LAP SHEAR TEST OF COPPER PLATED MAGNESIUM ALLOY LA-141 USING
A MODIFIED ZINCATE BATH

<u>Specimen Number</u>	<u>Area (In.²)</u>	<u>Load (lbs.)</u>	<u>Tensile Strength (psi)</u>
1	.5000	960	1920
2	.5000	275	550
3	.5000	195	390
4	.5000	190	380

TABLE II. - LAP SHEAR TEST OF COPPER PLATED MAGNESIUM ALLOY LA-141 USING
A CONVENTIONAL ZINCATE BATH

<u>Specimen Number</u>	<u>Area (In.²)</u>	<u>Load (lbs.)</u>	<u>Tensile Strength (psi)</u>
1	.5000	70	140
2	.5000	130	260
3	.5000	230	460
4	.5000	210	420

TABLE III. - LAP SHEAR TEST OF COPPER PLATED MAGNESIUM ALLOY LA-141
USING A FIVE PERCENT NITRIC ACID PREPLATING PICKLE

<u>Adhesive</u>	<u>Area (In.²)</u>	<u>Load (lbs.)</u>	<u>Strength (psi)</u>
934	.7340	915	1231
Lefkowl 109/LM52	.6562	1180	1798
MS 907	.7031	1050	1493
BC 2132	.6250	940	1504

TABLE IV. - TENSILE TEST OF COPPER PLATED MAGNESIUM ALLOY LA-141 USING
A SIX PERCENT NITRIC ACID PREPLATING PICKLE. SPECIMENS WERE
JOINED BY ORGANIC ADHESIVES.

<u>Adhesive</u>	<u>Area (In.²)</u>	<u>Load (lbs.)</u>	<u>Strength (psi)</u>
1-100	1.0000	1755	1755
907	1.0000	3940	3940
828	1.0000	860	860

TABLE V. - TENSILE TEST OF COPPER PLATED MAGNESIUM ALLOY LA-141 USING A SIX PERCENT NITRIC ACID PREPLATING PICKLE. SPECIMENS WERE JOINED BY SOLDERING.

<u>Specimen Number</u>	<u>Area (In.²)</u>	<u>Load (lbs.)</u>	<u>Strength (psi)</u>
1	1.0000	8175	8175
2	1.0000	5465	5465
3	1.0000	5205	5205
4	1.0000	3605	3605

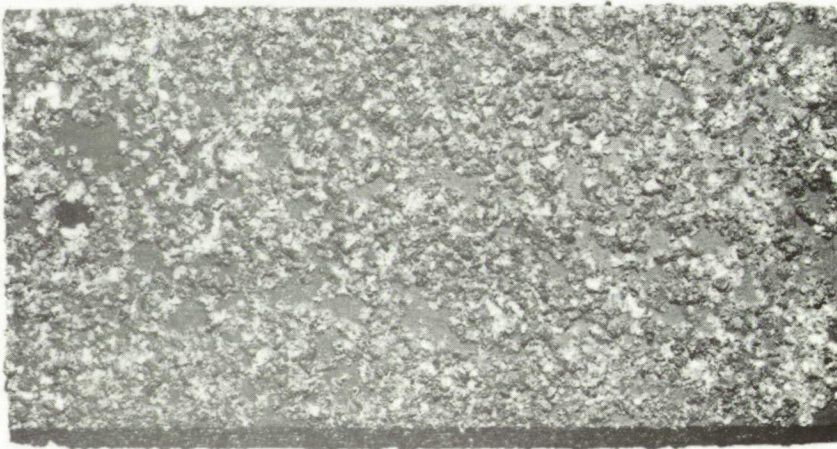
TABLE VI. - TENSILE TEST OF COPPER PLATED MAGNESIUM ALLOY AZ31B USING THE CONVENTIONAL "DOW" PROCEDURE. SPECIMENS WERE JOINED BY SOLDERING.

<u>Specimen Number</u>	<u>Area (In.²)</u>	<u>Load (lbs.)</u>	<u>Strength (psi)</u>
1	1.0000	5940	5940
2	1.0000	4220	4220
3	1.0000	2260	2260
4	1.0000	* -	-

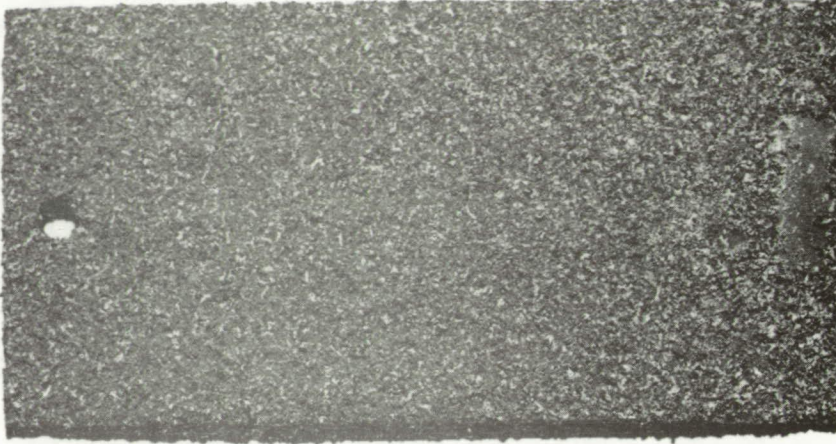
* Specimen was broken before tensile test was performed.



AZ31B

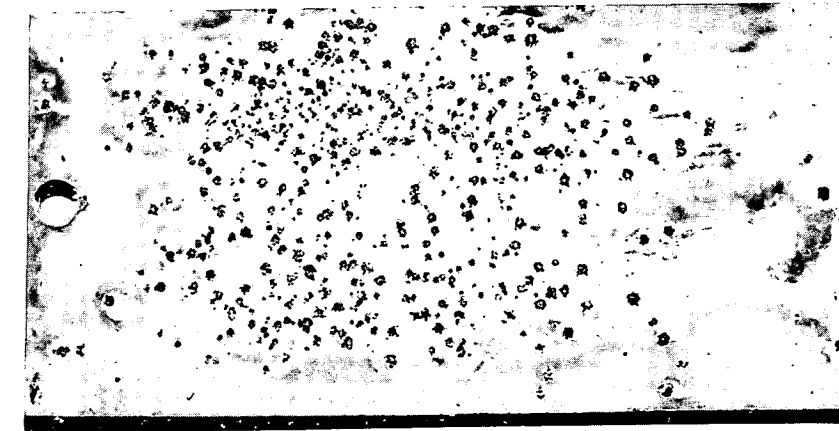


LA-141

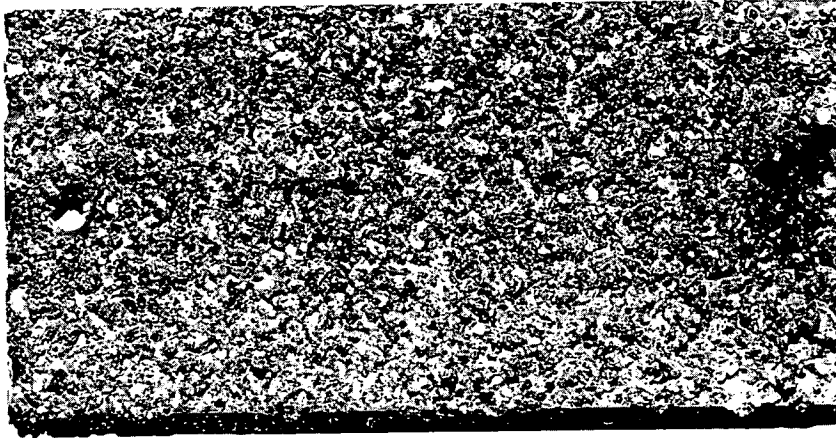


LAZ-933

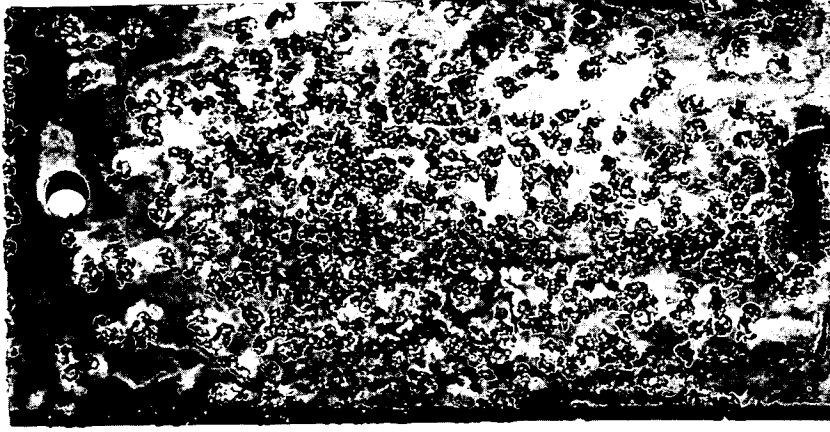
FIGURE 1 - SALT SPRAY TESTS OF GOLD PLATED MAGNESIUM ALLOYS. EXPOSURE TIME - 4 HOURS



AZ31B



LA-141

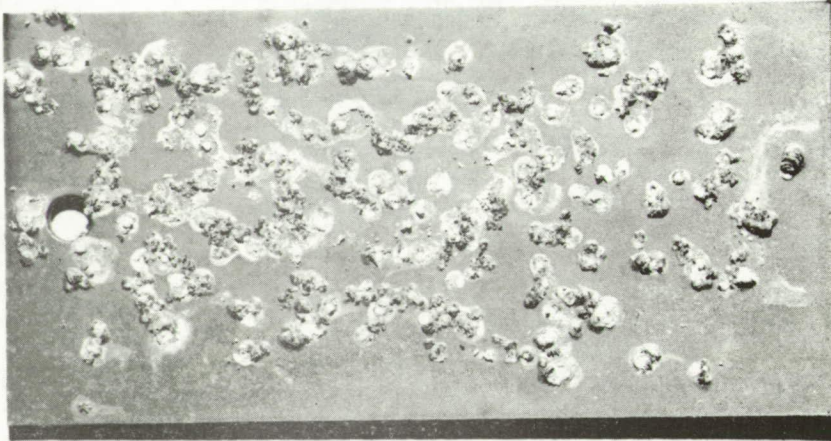


LAZ-933

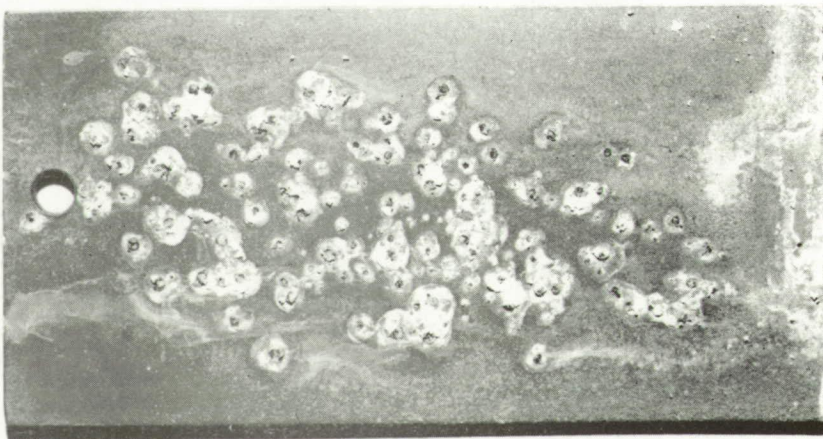
FIGURE 2 - SALT SPRAY TESTS OF CADMIUM PLATED MAGNESIUM ALLOYS. EXPOSURE TIME - 4 HOURS



L A Z - 933



L A - 141



A Z 31 B

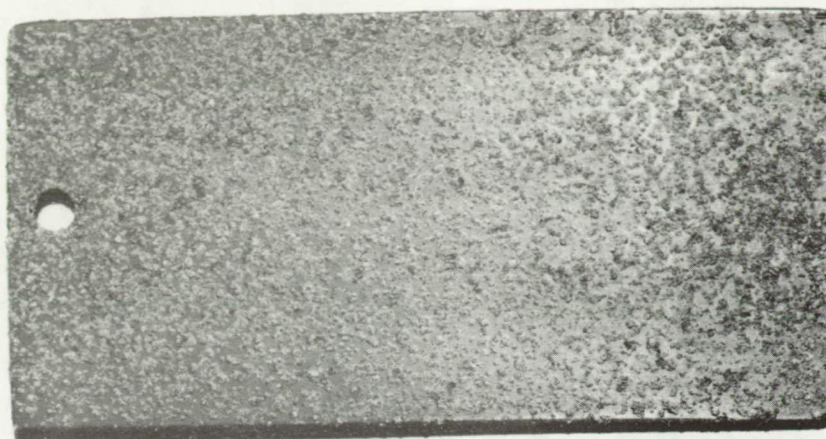
FIGURE 3 - SALT SPRAY TESTS OF NICKEL PLATED MAGNESIUM ALLOYS. EXPOSURE TIME - 4 HOURS



AZ31B

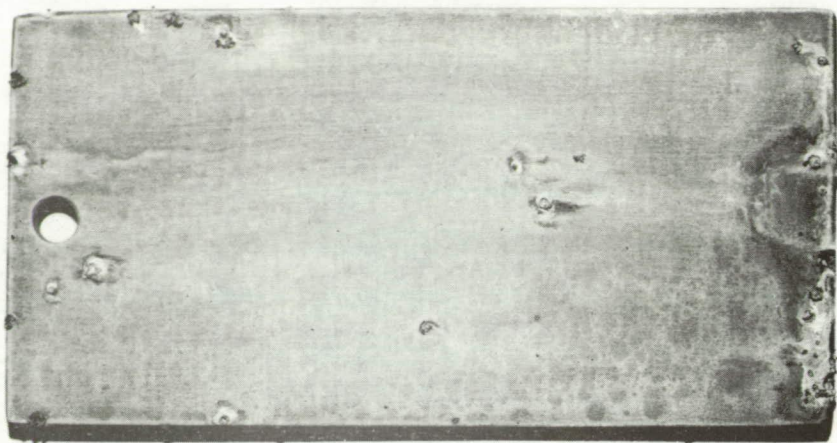


LA-141

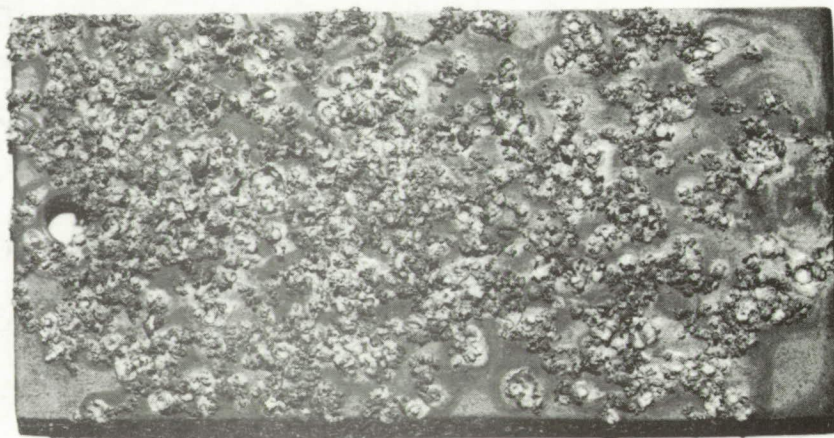


LAZ-933

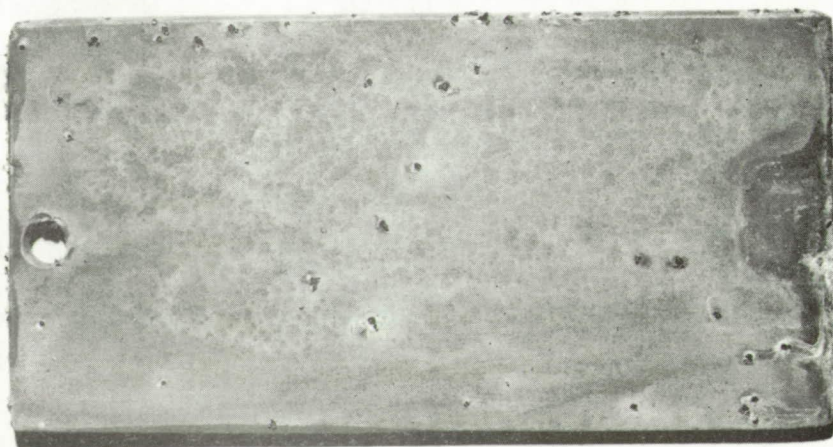
**FIGURE 4 - SALT SPRAY TESTS OF GOLD PLATED MAGNESIUM
ALLOYS. EXPOSURE TIME - 1 HOUR**



LAZ-933



LA-141



AZ31B

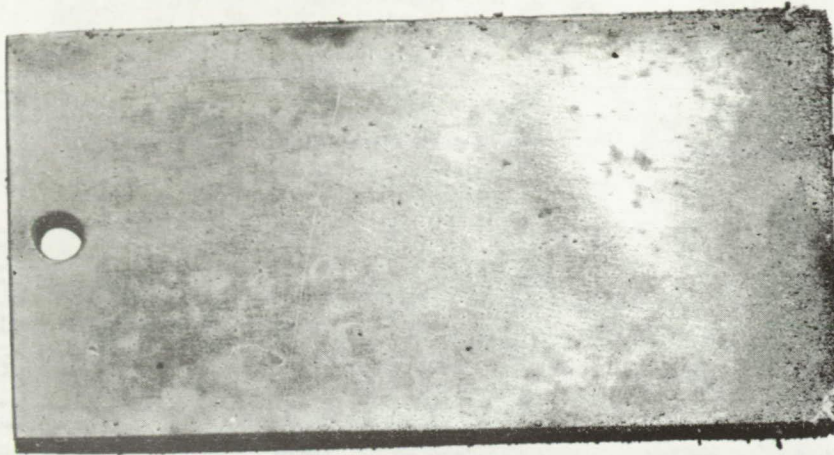
FIGURE 5 - SALT SPRAY TESTS OF CADMIUM PLATED MAGNESIUM ALLOYS. EXPOSURE TIME - 5 HOURS



AZ31B



LA-141

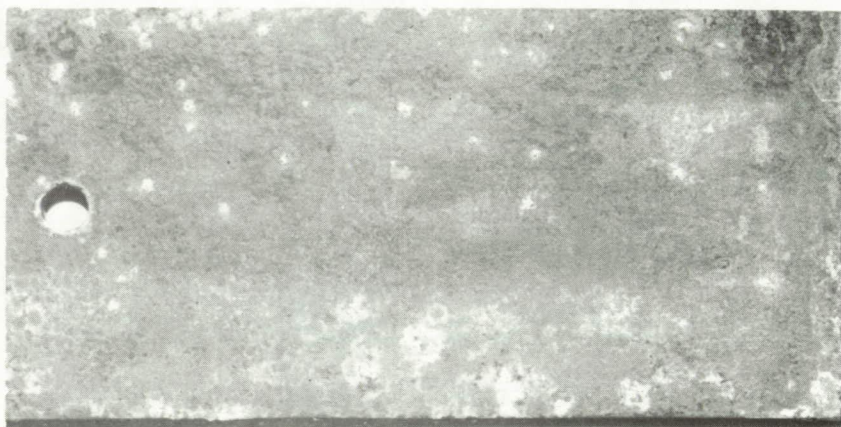


LAZ-933

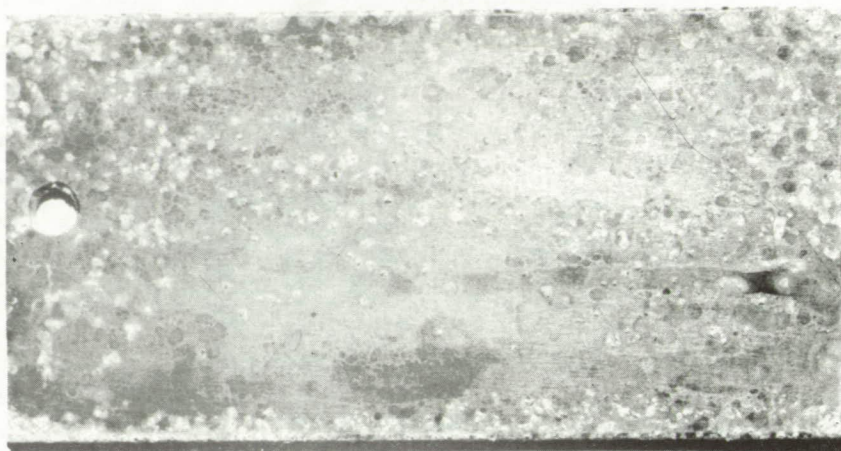
**FIGURE 6 - SALT SPRAY TESTS OF NICKEL PLATED MAGNESIUM
ALLOYS. EXPOSURE TIME - 5 HOURS**



AZ31B

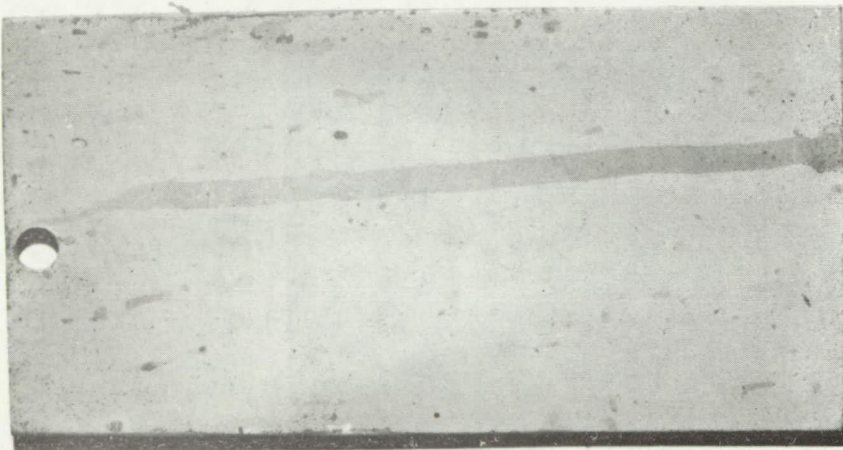


LA-141

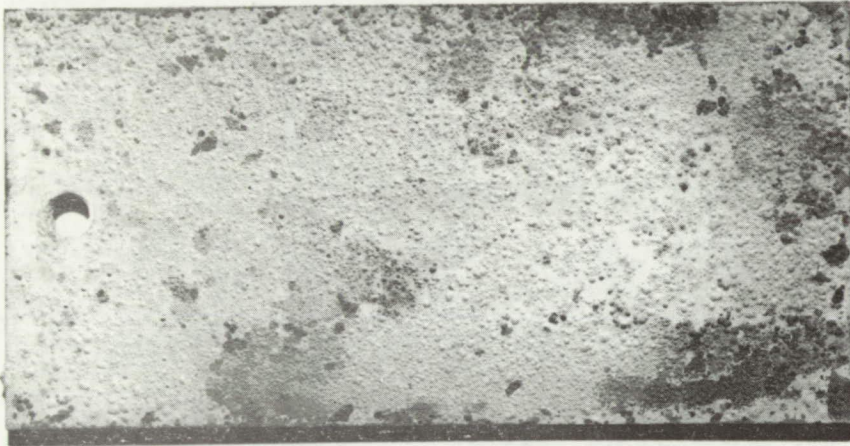


LAZ-933

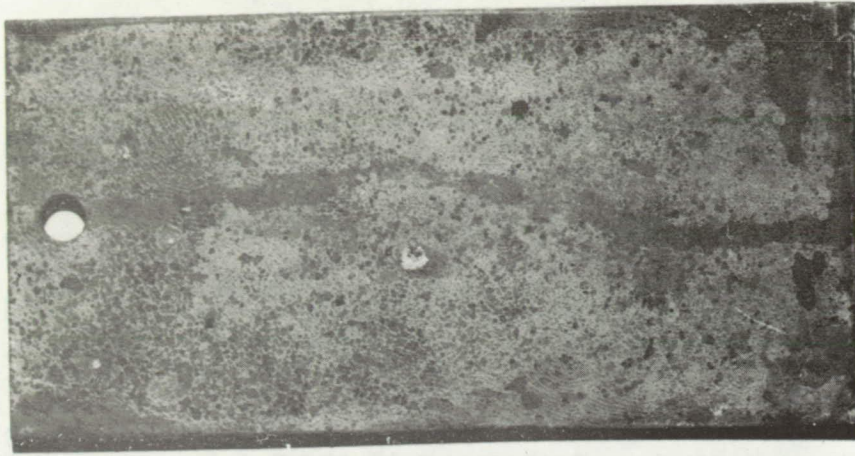
**FIGURE 7 - ENVIRONMENTAL TESTS OF GOLD PLATED MAGNESIUM
ALLOYS. EXPOSURE TIME - 336 HOURS**



AZ31B

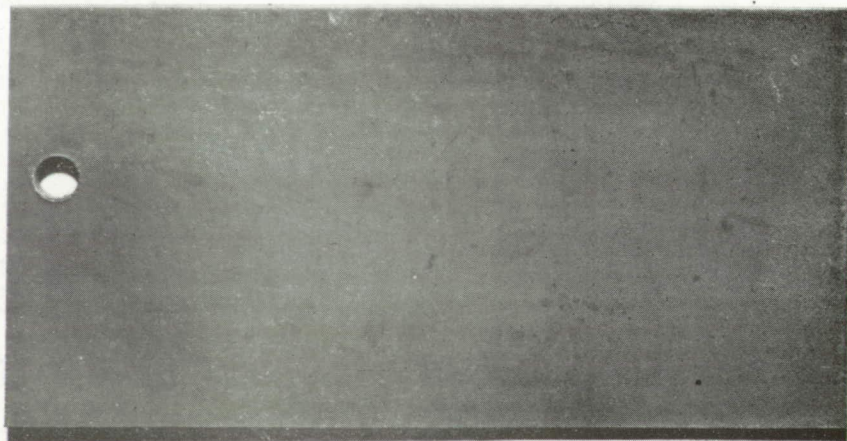


LA-141



LAZ-933

FIGURE 8 - ENVIRONMENTAL TESTS OF CADMIUM PLATED MAGNESIUM ALLOYS. EXPOSURE TIME - 336 HOURS



AZ31B

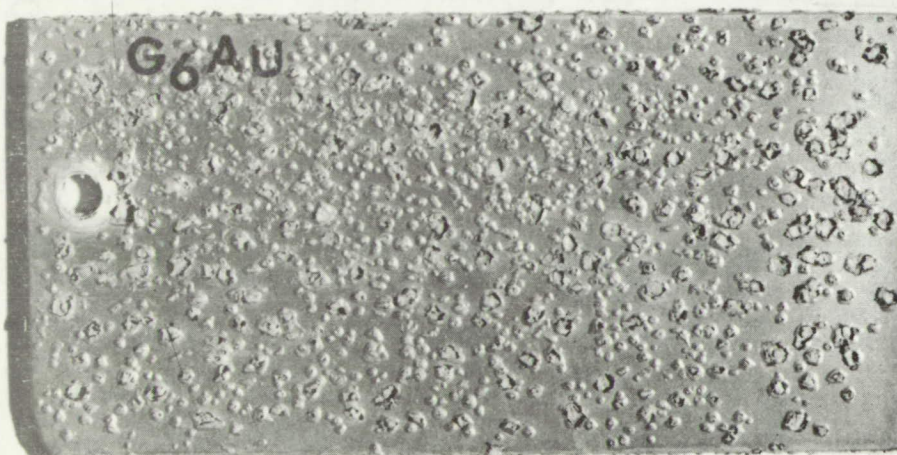


LA-141

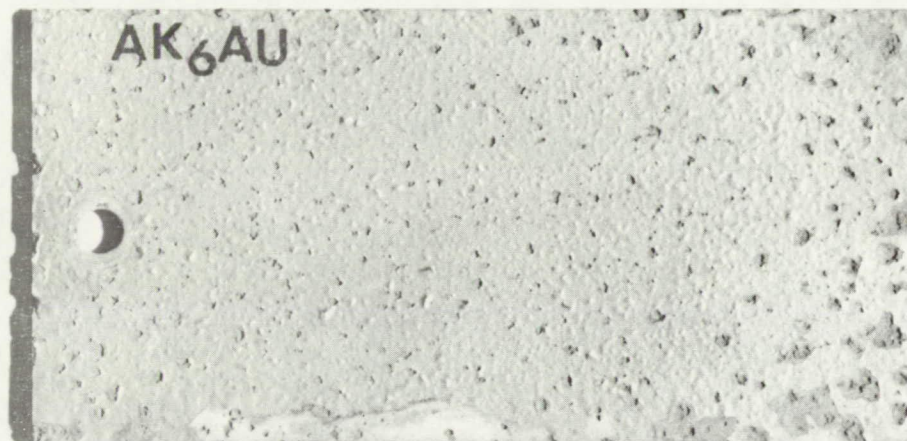


LAZ-933

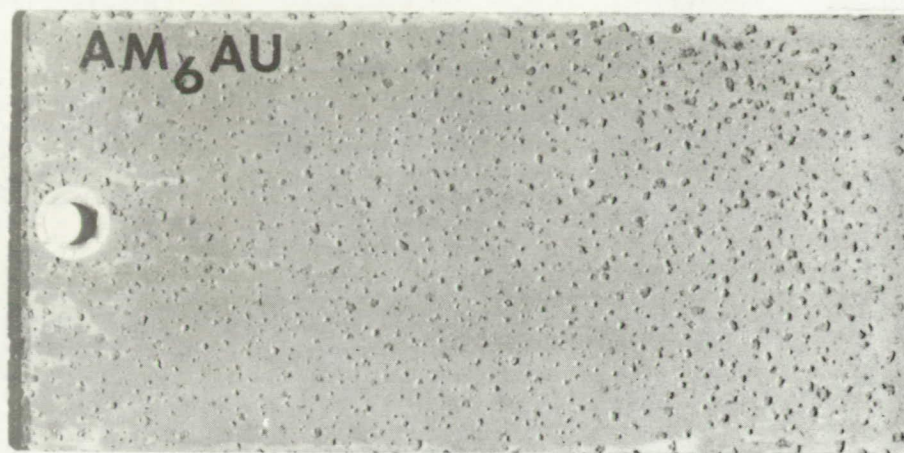
**FIGURE 9 - ENVIRONMENTAL TESTS OF NICKEL PLATED MAGNESIUM
ALLOYS. EXPOSURE TIME - 336 HOURS**



AZ31B

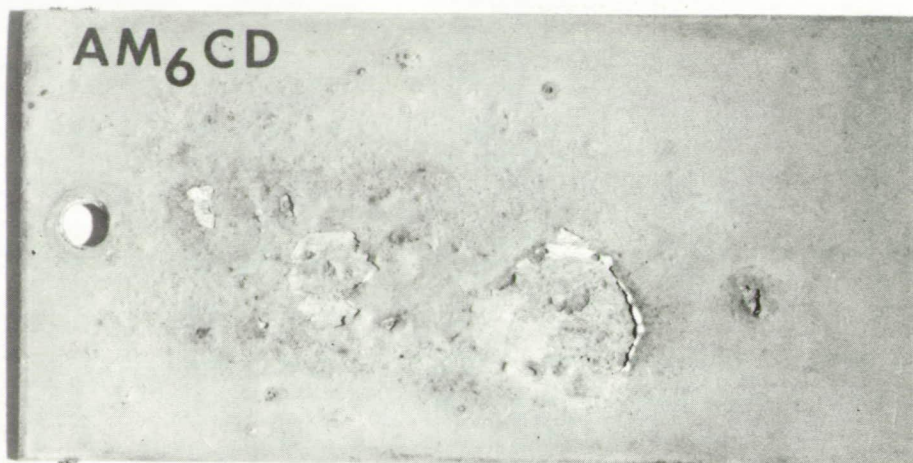


LA-141



LAZ-933

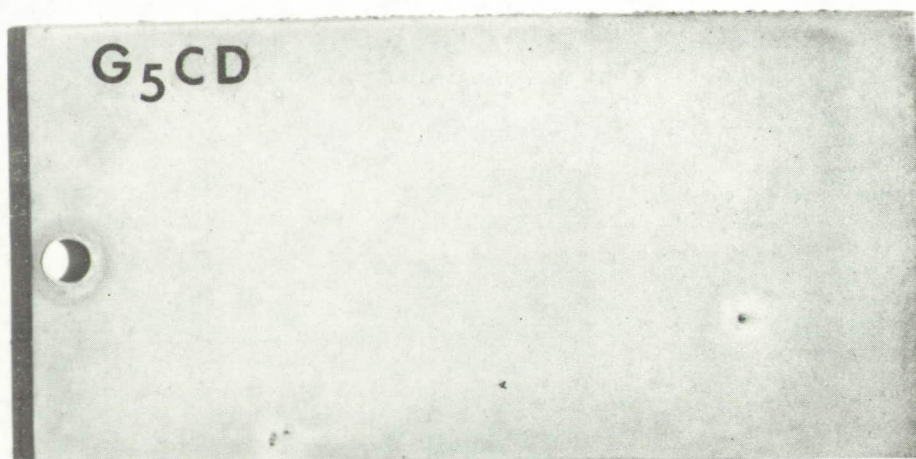
**FIGURE 10 OUTDOOR EXPOSURE TESTS OF GOLD PLATED MAGNESIUM ALLOYS.
EXPOSURE TIME - 18 MONTHS**



L A Z - 933

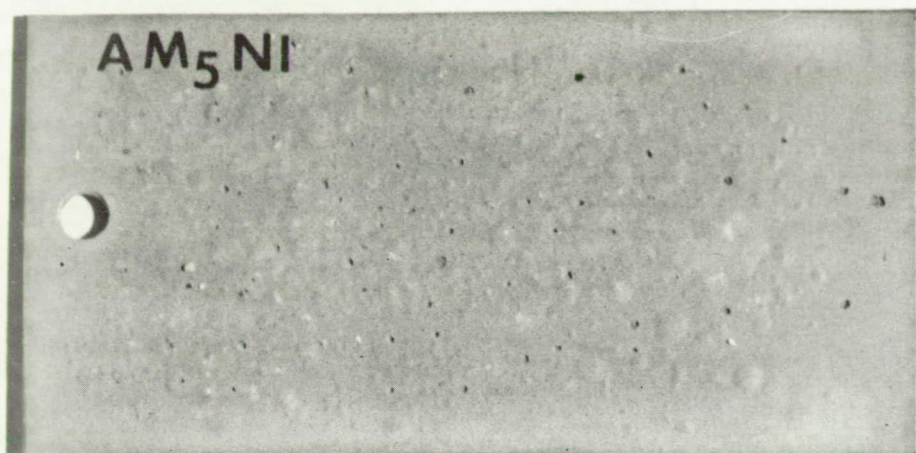


L A - 141



A Z 31 B

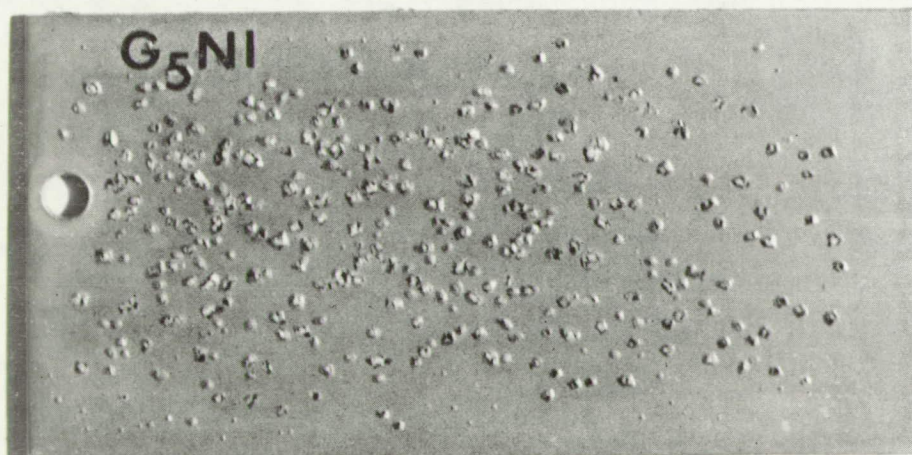
**FIGURE 11 OUTDOOR EXPOSURE TESTS OF CADMIUM PLATED MAGNESIUM ALLOYS.
EXPOSURE TIME - 18 MONTHS**



LAZ933



LA-141



AZ31B

FIGURE 12 OUTDOOR EXPOSURE TESTS OF NICKEL PLATED MAGNESIUM ALLOYS.
EXPOSURE TIME - 18 MONTHS

December 5, 1968

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INVESTIGATION OF ELECTROPLATING PROCEDURES FOR
MAGNESIUM LITHIUM ALLOYS

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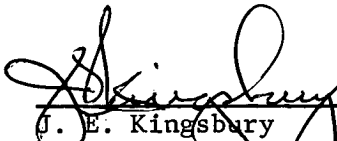
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